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Synthesis, characterization and kinetics of epitaxial-oriented silicon nanowire arrays on Si substrates

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Abstract

The fabrication of vertical-oriented, high aspect ratio silicon nanowires (SiNWs) with controllable density and length is of interest for the development of nanowire-based electronics and photovoltaic devices. Here we reported a both simple and economical method for synthesizing large-area epitaxial-oriented SiNW arrays, which was achieved on the Si (111) substrates by Au catalyzed vapor-liquid-solid mechanism using the conventional chemical vapor deposition furnace system. Their morphologies and microstructures were investigated with scanning electron microscopy and transmission electron microscopy, respectively. The results showed that most of nanowires were vertically grown on substrates, their density and length can be well controlled. As-grown SiNW is composed of a single crystalline silicon core and a thin amorphous silicon oxide coating layer. Furthermore, their growth kinetics was discussed in detail. It indicates that there are both the substrate-nanowire Si adatom surface diffusion and the slight radial growth during the upgrowth of nanowire, and besides, the migration of Au on the sidewall of nanowire was also found for such epitaxial-oriental SiNWs.

PACS:

Keywords: *Silicon nanowire; Epitaxial growth; Chemical vapor deposition; Microstructure; Surface diffusion*

Introduction

It is well known that the integrated-circuit (IC) industry is developing towards creating smaller and faster components that are of less production cost [1]. On the other hand, SiNWs have the unique structures and properties [2], and also have the advantage of the currently IC technical compatibility, compared with other semiconducting nanowires. And hence SiNWs have been attracting a lot of attention for numerous potential applications in nanoelectronics devices [3, 4], or in the emerging application areas of photonics [5], chemical sensors [6], lithium-ion batteries [7], and solar cells. Recently, many synthesis techniques have been exploited for the growth of SiNWs

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[8], such as the metal-catalytic/catalyst-free chemical vapor deposition (CVD) method, the laser ablation method, the oxide-assisted growth and the solution-based synthesis method. Among these method, metal-catalytic CVD technique via the vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) mechanism have been widely used since Wagner et al reported the first silicon whiskers synthesized by Au-catalyzed VLS growth four decades ago [9]. However, this method usually produced randomly oriented SiNWs that require further assembling procedure to make devices on substrates [2, 10]. The fabrication of vertical-oriented, high aspect ratio SiNWs with controllable density and length is therefore of interest for the development of nanowire-based electronics and photovoltaic devices.

In the past ten years, many efforts have been made to directly synthesize vertical-oriented SiNWs. Especially, several studies have reported the use of alternative metal as catalyst for the growth of vertical-oriented SiNWs via the self-oriented epitaxy technique [11]. For example, Hannon et al [12] demonstrated that the vertical-oriented SiNWs were synthesized on Si (111) wafer by Au-catalyzed VLS epitaxy in the ultrahigh vacuum (UHV) CVD system. Subsequently, Wang et al [13] also fabricated the vertical-oriented SiNWs on the Si (111) wafer by Al-catalyzed VSS epitaxial-growth using the similar system. However, for the above self-oriented SiNWs, the facts of lower growth rate (~ 20-100 nm/min) and higher production cost limit its application prospects as the electronic or photovoltaic materials. Consequently, the approaches that are of more economic and efficient have been pursued for vertical-oriented SiNWs. Fan et al [14] firstly demonstrated that the orientation-controlled growth of silicon nanowire (SiNW) arrays were achieved by Au catalyzed VLS growth on Si substrates in a conventional CVD furnace system. And then the vertical-oriented SiNW arrays were also synthesized on Si (111) wafer by Pt (and Al) catalyzed VLS growth in the similar experimental setup [15, 16]. Such SiNWs are usually of high growth rate in the range from several to several hundred micrometers. Unfortunately, there is the disadvantage of lower repeatability and higher density for such SiNW arrays, which was attributed to the precursor concentration and supersaturation increasing induced by the larger gas flow flux and the higher gas pressure during the consecutive growth processes, respectively.

In this paper, we have demonstrated a both simple and promising method for synthesizing large-area epitaxial-oriented SiNW arrays with controllable morphology and density on Si (111) wafers by Au catalyzed VLS growth using H_2 and SiH_4, which was achieved by using a rotary-pumped CVD furnace system equipped with a quartz-tube. Their morphology and microstructure were investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with an energy dispersive X-ray (EDX) system, respectively. Furthermore, the growth kinetics of as-grown epitaxial-oriental SiNWs was discussed in detail.

2. Experimental

Large-area epitaxial-oriented SiNW arrays were synthesized on Si (111) wafers by the conventional CVD process. Prior to the SiNWs growth, the Si wafers were firstly cleaned and degreased with a 10:1 (v:v) H_2SO_4 : H_2O_2 solution (100°C), and then immersed in dilute HF acid for 1min to remove native oxides, followed by rinsing with deionized water and drying with nitrogen. Subsequently, a thin film of Au that is served as the catalyst, was deposited onto the HF-treated Si wafers using the magnetron sputtering method for about 15-60sec, the corresponding thickness of film is estimated to be about 5-20nm, respectively.

The Si (111) wafers coated with the different thicknesses of Au films were placed together into a ceramic boat, which was inserted into the center of the horizontal quartz-tube inside a CVD furnace. The whole vacuum system began to be pumped by a rotary pump until its vacuum reached about 1Pa. After that, the furnace temperature was increased at a rate of about 10°C/min from 20°C to 540°C, and of 3°C/min from 540°C to 600°C. During this process, the protecting H_2 flow rate of 20sccm (standard cubic centimeters per minute) was initiated into the quartz-tube after the furnace temperature reached about 300°C, and furthermore, the thin Au film was transformed into nanoparticles with the average size of about 150-250nm. When the temperature of furnace just reached 600°C, the SiH_4 was flowed into the furnace tube at a flow rate of 2-5sccm and maintained at this temperature for 1h. During the reactive process, the total growth pressure was varied from 20Pa to 5000Pa, and even higher, the flow ratio of SiH_4 and H_2 was varied from 1:2 to 1:8, respectively. After that, the SiH_4 was firstly turned off and the furnace temperature was cooled to room temperature naturally. The protecting H_2 flow of 20sccm was turned off after the furnace temperature is less than 300°C.

The morphologies of as-grown epitaxial-oriented SiNW arrays were initially examized by the SEM observation. To investigate the growth kinetics of such epitaxial SiNWs, we first studied the effects of the related experiment parameters on the growth of SiNW arrays, and then we performed the TEM studies for the individual SiNW. As-grown SiNWs were firstly transferred into ethanol, and then dropped onto a copper grid with a holey carbon film support. High-resolution TEM (HRTEM) imaging of individual SiNW together with

the EDX analysis were carried out on a JEM-2100F TEM system operated at accelerating voltage of 200KV. The images were recorded with a Gatan 832 CCD camera.

3. Results and discussions

Epitaxial-oriental SiNW arrays have been successfully synthesized on the Si (111) substrates by Au catalyzed growth. Fig.1(a)-1(d) show the typical SEM images (taken with the sample stage by 45°) of the as-grown SiNW arrays catalyzed with the Au film of different thicknesses, which were synthesized at 600°C for 1h with the total gas pressure of 100Pa using the H_2 and SiH_4 flow flux of 16sccm and 4sccm. First, as-grown SiNWs have the uniform distribution and morphology, and their diameters are measured to be about 200nm in average. However, there are a few nanowires with the diameters of less than 100nm or of larger than 250nm. Second, most of the SiNWs are perpendicular to the Si (111) substrates, as verified by the top-view SEM images shown in Fig.2(a)-2(d), in which the vertical SiNWs are the light spots. The statistical results indicate that there are about 75 percent of the SiNWs that were vertically grown on the substrates, and the percentage of the vertical nanowires is almost independent on the thickness of Au catalyst. And besides, those nanowires that were not perpendicular to the Si substrates nearly form the triangular networks according to the observation from the Fig.2(a)-2(d). Therefore, it is an epitaxial growth process for these self-oriented SiNWs grown on the Si (111) substrates and their growth axis should be along <111> directions [14]. Three, there is an obvious dependence of the nanowire density on the thickness of Au film for as-grown SiNW arrays, that is, the density almost increases linearly from about $1.5\times10^5/mm^2$ to $6.1\times10^5/mm^2$ with the Au catalyst deposition time increasing from about 15sec to 60sec. And finally, such epitaxial-oriental SiNW arrays can be well repeated under the same experimental parameters in random growth process. It indicates a negligible silicon deposition on the sidewall of the quartz-tube during the reactive process [14].

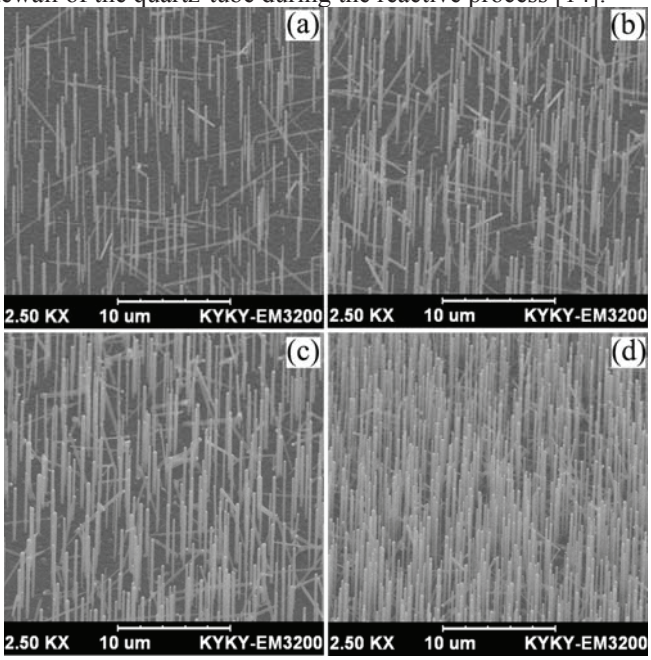


Fig.1. 45° angle view SEM images of vertical SiNW arrays epitaxial-grown on Si (111) substrates with the different Au catalyst deposition times of (a) 15sec, (b) 30sec, (c) 45sec, and (d) 60sec.

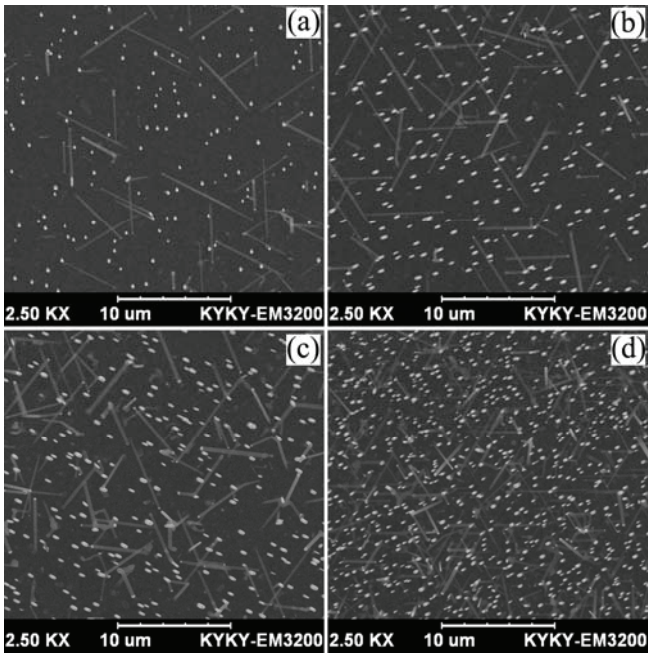


Fig.2. The top-view SEM images of vertical SiNW arrays epitaxial-grown on Si (111) substrates with the different Au catalyst deposition times of (a) 15sec, (b) 30sec, (c) 45sec, and (d) 60sec.

It is worthwhile to mention that the orientation-controlled epitaxial growth of SiNW arrays with both the uniform distribution and the well repeatability can be achieved at quite wide growth conditions, where the growth pressure can be varied from 20Pa to 5000Pa, the total gas flow flux of H_2 and SiH_4 can be varies from 10sccm to 25sccm, the best ratio of H_2 and SiH_4 is in the range from 3.5:1 to 4.5:1, and the best growth temperature is about 600±20°C. Note that these results was summarized according to abundant experiments and corresponding SEM observations. In the following, we mainly discussed the effects of total growth pressure and total gas flow flux on the length of as-grown SiNWs synthesized under the best growth temperature of 600°C and the moderate H_2 and SiH_4 ratio of 4:1.

Fig.3 (a) shows the dependence of the length on the total gas pressure for the epitaxial-oriented SiNWs synthesized with the H_2 and SiH_4 flow flux of 16 sccm and 4 sccm. Its growth rate first increases quickly from about 2.7μm/h to 6.5μm/h with total gas pressure increasing from 20Pa to 100Pa, and then increases slowly with the continuous increase of total gas pressure, and finally nearly reaches the saturation (~7.8μm/h) after the total gas pressure exceeds 1000Pa. It is an obvious nonlinear behavior between them. However, there is a nearly linear relationship between the growth rate and the total gas flow flux, as shown in Fig.3 (b). It shows the dependence of the length on the total gas flux for the epitaxial-oriented SiNWs synthesized at the gas pressure of 500Pa. Such linear relationship provides us a simple method for controlling the length of as-grown SiNWs.

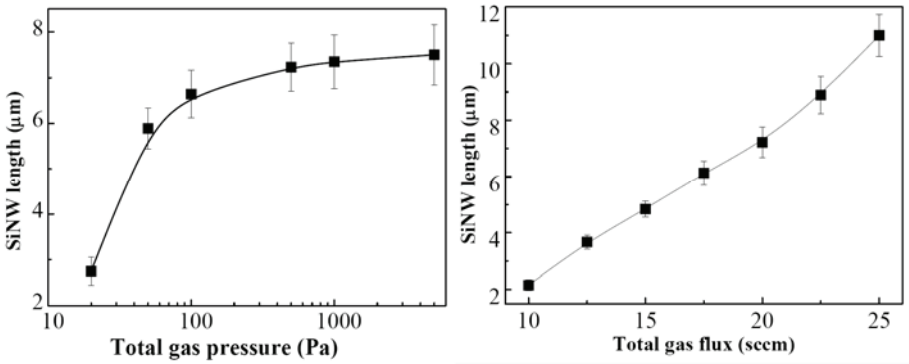
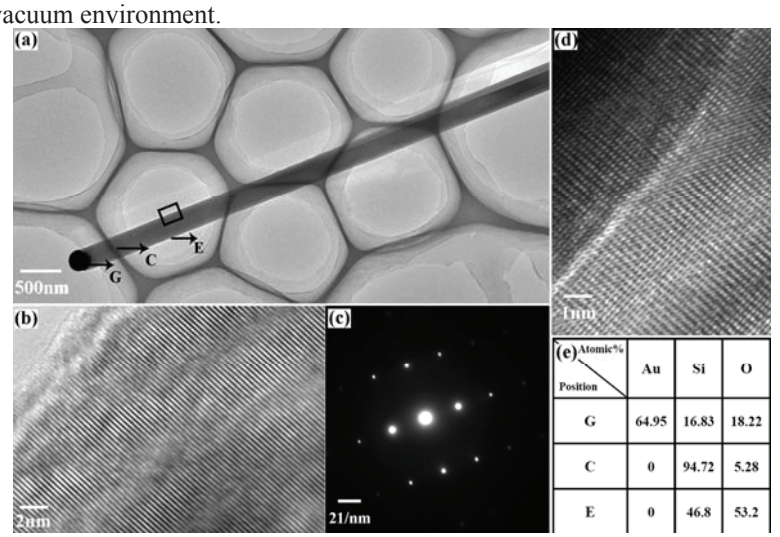


Fig.3. Length of SiNWs versus (a) total gas pressure and (b) total gas flow flux.

According to above discussions about the effects of the Au catalyst thickness and the related experimental parameters (including total gas pressure and total gas flow flux) on the growth and morphology for as-grown self-

oriented SiNW arrays, we can conclude that their density and length can be well controlled by adjusting the thickness of Au film deposited on the Si substrates and the total gas flow flux of H_2 and SiH_4, respectively. In order to thoroughly investigate their microstructures and growth kinetics of such epitaxial SiNWs, a detailed TEM studies have been performed for the individual nanowire.

Fig.4 (a) shows the HRTEM image of a typical SiNW with a larger diameter of about 270nm, and the central regions of the framed area are enlarged and shown in Fig.4 (b) together with the corresponding defocused selected area electron diffraction (SAED) shown in Fig.4(c). The SiNW is composed of a single crystalline silicon core and an amorphous outer layer with thickness of about 2nm and the long axis of the nanowire is nearly parallel to the <111> direction (as shown in Fig.4 (b)), which is in agreement with the deduction from the SEM observation. Alloy globule of Au-Si was formed and capped on the nanowire top, the HRTEM image of the catalyst-nanowire interface shown in Fig.4 (d) clearly indicates that Au has operated as a VLS catalyst. In other words, the growth of Au-catalyzed SiNWs followed a VLS mechanism, as verified by the former studies of self-oriented SiNWs [17]. On the other hand, the results from the EDX analysis were shown in the table of Fig.4 (e), which lists the atomic percent of Au, Si and O at three different regions marked in Fig.4 (a) with the capital letter of "G", "C", and "E". Note that these capital letters are the shortened forms of the Au-Si alloy globule, the central area and the edge area of nanowire, respectively. It shows that the core is mostly composed of silicon, and the thin outer layer is mostly composed of amorphous SiO_x ($1<x<2$). Moreover, the HRTEM analyses confirmed that there was nearly the same thickness (~2nm) for the different parts of whole nanowire, and hence the amorphous outer layer was not formed together with the upgrowth of nanowire, but formed during the subsequent cooling process due to the surface oxidizing in the low vacuum environment.



(e)

Atomic% / Position	Au	Si	O
G	64.95	16.83	18.22
C	0	94.72	5.28
E	0	46.8	53.2

Fig.4. (a) HRTEM image of a typical SiNW, (b) the magnified image of the framed central region marked in panel a, (c) the corresponding defocused SAED pattern. (d) HRTEM of interfaces between the alloy globule and nanowire, (e) A table listing the atomic percent of Au, Si and O at the different regions marked in panel a with "G", "C", "E", respectively.

For the growth of such epitaxial-oriented SiNWs, the HRTEM analyses from the whole nanowire shown in Fig. 5 (a) indicate that there were the radial growth existed together with the migration of Au on the nanowire sidewall, besides the axial growth induced by Au catalyzed VLS mechanism. Its diameter first slowly increases from about 100nm to about 150nm and then quickly decreases to ~100nm from the nanowire tip to the nanowire base, and the region with the largest diameter is almost in a distance of about 1.5μm from the bottom of nanowire. This characteristic has been also verified by the SEM observations. The radial growth results in the increase of diameter for as-grown nanowires. Moreover, their surface usually becomes rougher and rougher with the increase of nanowire diameter and the region with the largest diameter has the roughest surface, as shown in Fig. 5 (b). These protuberances on the rough surface can be attributed to the migrated Au catalyzed VLS growth [12]. For the bottom of nanowire, on the other hand, the decrease of diameter should be related with the surface diffusion of Si adatom between the substrate and nanowire [18]. The substrate-nanowire Si adatom exchange can held back the migrated Au catalyzed VLS growth on the sidewall of nanowire base, and hence there is a relatively smooth surface for the

nanowire base, as shown in Fig. 5 (b). This primary understanding will allow us to obtain more favorable control over the Au catalyzed epitaxial-oriented SiNWs vertical-grown on the Si (111) substrates.

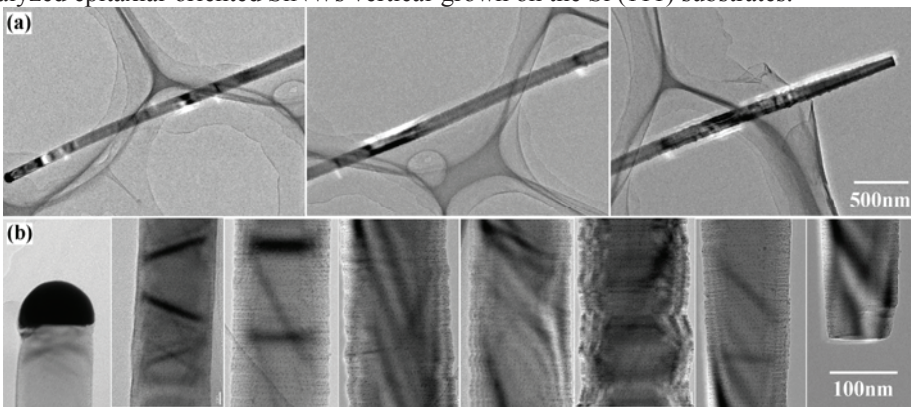


Fig.5. (a) HRTEM images of a whole SiNW, (b) the higher-resolution TEM images of different segments for an individual SiNW.

Conclusion

A both practical and promising method has been reported for the growth of large-area epitaxial-oriented SiNW arrays, which was synthesized on Si (111) wafers by Au catalyzed VLS mechanism in the conventional CVD process. There are about 75 percent of the SiNWs vertical-grown on substrates. Their density and length can be well controlled by adjusting the thickness of Au film deposited on substrates and the total gas flow flux of H_2 and SiH_4 during the reactive process, respectively. The results from the HRTEM and EDX analyses indicate that such self-oriented nanowire is composed of a single crystalline silicon core with the (111) orientation and an amorphous SiO_x coating layer with the thickness of about 2nm. Besides the axial growth, moreover, there is the substrate-nanowire Si adatom surface diffusion and the radial growth together with the migration of Au on the sidewall of nanowire. This primary understanding will allow us to obtain more favorable control over the Au catalyzed epitaxial-oriented SiNWs on Si substrates for such simple method.

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